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Dielectric properties of sol-gel derived barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$) ceramics

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Abstract : A series of $Ba_{1-x}Sr_xTiO_3$ (x = 0.0, 0.1, 0.2, ..., 1.0) ceramics have been fabricated by sol-gel processing technique. The structural properties of the ceramics have been reported. The ceramic samples tend to be cubic in structure except for x = 0.0, 0.1 and 0.2 for which the structures are tetragonal. At room temperature, the sample with x = 0.2 has the maximum value of dielectric constant and minimum value of loss tangent with the values reported as 1435 and 0.013 respectively at 1KHz frequency. The dielectric properties of the ceramics have been reported both as a function of frequency and temperature for different compositions. The dielectric constant ϵ' shows a slight frequency dispersion at the lower frequency edge while the loss tangent shows small frequency dispersion at higher frequencies. There is a systematic decrease in the value of the transition temperature of the ceramics with increase in the value of x. The phase transitions are found to become more and more diffuse with the increase of the value of x.

Keywords : Ferroelectric ceramics, dielectric constant, sol-gel technique

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1. Introduction

There has been considerable interest in ferroelectric ceramics due to the possible applications in piezoelectric [1], pyroelectric [2], electro-optic [3], acousto-optic [4] and memory [5] devices. Ceramic capacitors derive their high capacitance per unit volume from the high dielectric constants found in ferroelectric materials. Ferroelectric materials have been used in both non-volatile and volatile memories [6, 7]. However, major effort has been given towards lead based perovskites such as lead-zirconate titanate ($Pb(Zr, Ti)O_3$ or PZT), lead titanate ($PbTiO_3$) *etc*. Solid state reaction technique as well as sol-gel technique have been successfully used for the synthesis of the above materials. Although PZT has excellent properties for low frequency applications, this material has serious problem of fatigue (in the case of switching applications), serious degradation of the dielectric properties at a few megahertz frequencies. Now the focus is shifting towards the non-lead based perovskites such as barium titanate ($BaTiO_3$), barium strontium titanate ($(Ba,Sr)TiO_3$ or BST). Barium titanate has been extensively used as the ferroelectric ceramic material. However, this material has a big disadvantage of high transition temperature (T_c) of about 398K [7] at which the dielectric constant is maximum. It has long been known that the substitution of strontium atoms for some atoms of barium in barium titanate can lowers the transition temperature [8] to the order of room temperature. In the ceramic form, the transition temperature of strontium titanate has been reported to be about 20K [9]. So, with the proper choice of Ba/Sr ratio the transition temperature of $Ba_{1-x}Sr_xTiO_3$ can be brought at or about the room temperature. Extensive studies have been made on the properties of barium strontium titanate ceramic prepared by solid-state-reaction method [9,10]. Recently, sol-gel technique have been utilised for the fabrication of BST powder and ceramic [11, 12]. In this process solution chemistry is used for the fabrication of the ferroelectric powder. The advantages of the sol-gel technique are easy composition control, low processing temperature, fine particle size, short fabrication cycle and ultra-homogenization of the product material due to atomic scale mixing of the components. In this paper, we report the fabrication of BST ceramics by sol-gel processing technique, structural characterisation of the samples and a study of their dielectric properties.

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2. Experimental

A series of barium strontium titanate [$Ba_{1-x}Sr_xTiO_3$ ($x = 0.0, 0.1, 0.2, \ldots, 1.0$)] ceramic samples were prepared by sol-gel processing technique taking barium acetate [$Ba(CH_3COO)_2$](E Merck, Germany), strontium acetate [$Sr(CH_3COO)_2$] (Aldrich) and titanium isopropoxide [$Ti(CH_3)_2CHO]_4$ as starting materials. Acetic acid [CH_3COOH] was used as solvent and 2-Methoxy ethanol [$CH_3(CH_2)OH$] was used as chemical modifier. Correct amounts of $Ba(CH_3COO)_2$ and $Sr(CH_3COO)_2$ were separately dissolved in heated glacial acetic acid [CH_3COOH]. The two solutions were mixed. The resultant solution was refluxed for 3 hours and cooled down to room temperature. Appropriate quantity of $[Ti(CH_3)_2CHO]_4$ was modified in excess of 2-methoxyethanol [$CH_3(CH_2)OH$] and the solution was also refluxed for 3 hours and cooled down to room temperature. The two precursor solutions were mixed and stirred thoroughly using magnetic stirrer for about half an hour. The solution was then filtered and the filtrate was left as stock solution. The stock solution was set aside for about a week. A humid white opaque gel was obtained. The gel was converted to brown powder after firing at 350°C for one hour in air. The powder was then annealed at 700°C for one hour in air for crystallization to get a white crystalline powder of the material. The powder was crushed and pellets of the ceramic samples were prepared by pressing uniaxially the powder in the form of circular discs, using a pressure of 1.25×10^4 kg. cm^{-2}, and sintering the samples at 1300°C inside a high temperature furnace for two hours in ambient air. A small quantity of polyvinyl alchohol was added to the powder as binder which burnt out in the process of sintering. The structural characterizations of the samples was carried out by taking X-ray diffraction (XRD) spectrum using a Philips (PW 1840) X-ray diffractometer. The dielectric properties of the ceramics were investigated by using a GR 1615A Capacitance bridge tuned by a detector of type GR 1232A tuned amplifier and null detector. The above measurements were carried out on the samples in the metal-ferroelectric-metal (MFM) configuration. The samples were prepared by electroding the sintered ceramic discs (about 1.2cm diameter and 0.15 cm thick) with silver paint on both faces.

3. Results and discussion

3.1 Structural properties :

The as-fired powders were found to be amorphous which crystallised to cubic and tetragonal BST powders depending on the Ba/Sr ratio after annealing at 700°C for one hour in air. The X-ray diffraction (XRD) patterns of $Ba_{1-x}Sr_xTiO_3$ ($x = 0.0$,

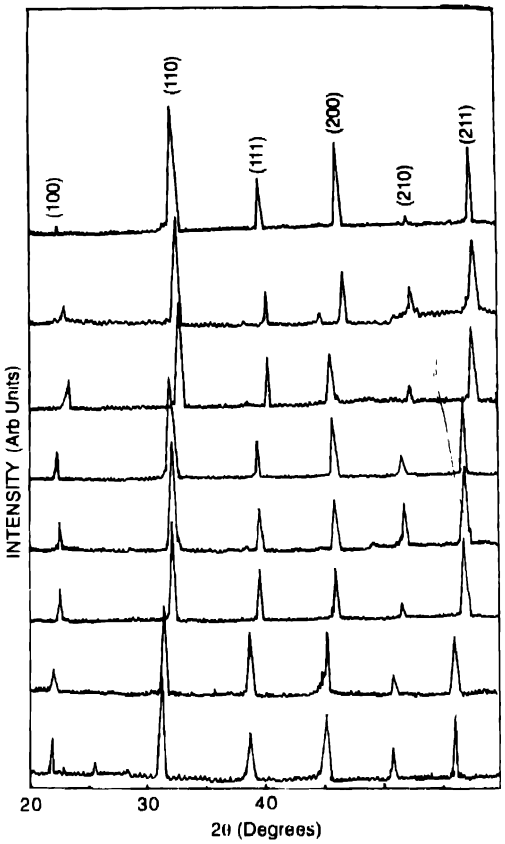

Figure 1. X-ray diffraction pattern of $Ba_{(1-x)}Sr_xTiO_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, 1.0$)

Table 1. Variation of lattice parameter, dielectric constant, loss tangent and transition temperature with x of $Ba_{1-x}Sr_xTiO_3$ ceramics

Value of x	Lattice parameters			Room temp. value (at 1KHz) of		Transition temperature (T_c) K
	a	b	c	ϵ'	$\tan\delta$	
0.0	4.003 ± 0.001	4.004 ± 0.001	4.040 ± 0.003	640	0.027	–
0.1	4.001 ± 0.001	4.001 ± 0.003	4.075 ± 0.006	1132	0.018	371
0.2	3.959 ± 0.003	3.965 ± 0.007	4.287 ± 0.009	1435	0.013	337
0.3	3.968 ± 0.007	3.977 ± 0.007	3.968 ± 0.003	1170	0.030	315
0.4	3.968 ± 0.001	3.969 ± 0.001	3.969 ± 0.000	704	0.051	281
0.5	3.916 ± 0.014	3.921 ± 0.001	3.924 ± 0.001	331	0.049	201
0.8	3.914 ± 0.006	3.912 ± 0.006	3.921 ± 0.008	53	0.055	-
1.0	3.909 ± 0.004	3.897 ± 0.004	3.902 ± 0.005	25	0.064	–

..0.2, ..., 1.0) are shown in Figure 1. The lattice parameters of he samples were calculated using the formula

$$1/d_{hkl}^2 = a^2/h^2 + b^2/k^2 + c^2/l^2 .$$

The lattice parameters of the ceramics of different compositions are shown in Table 1. The XRD study showed hat all the samples were single-phase cubic or tetragonal erovskite structure. All the samples with composition $x > 0.2$ howed cubic (Ba, Sr) TiO_3 structure while the samples with $x \leq 0.2$ are tetragonal. Similar results have been observed by earlier workers [9-15].

3.2 Dielectric properties :

Figures 2(a) and 2(b) show the room temperature variation of the dielectric constant (ϵ') and loss tangent ($\tan\delta$) of the samples of different compositions. As evident from Figure 2, at room temperature, the samples with composition $x = 0.2$ has a maximum dielectric constant with minimum loss tangent factor. Typical values of the dielectric constant and loss tangent for this composition measured at 1KHz were found to be 1435 and 0.013. Similar values of ϵ' have been reported by earlier workers for BST ceramics prepared by solid state reaction technique [14]. The value of $\tan\delta$ is slightly higher and ϵ' lower than that reported for BST ceramics [15]. This difference may be attributed to various factors such as stoichiometry, composition, porosity, grain size *etc*. However, a detailed study is needed to get a conclusive picture. The variations of the dielectric properties of the samples with frequency and temperature were also examined for all the samples. However, the result of the samples with $x = 0.2$ which shows a maximum dielectric constant is reported in the following section

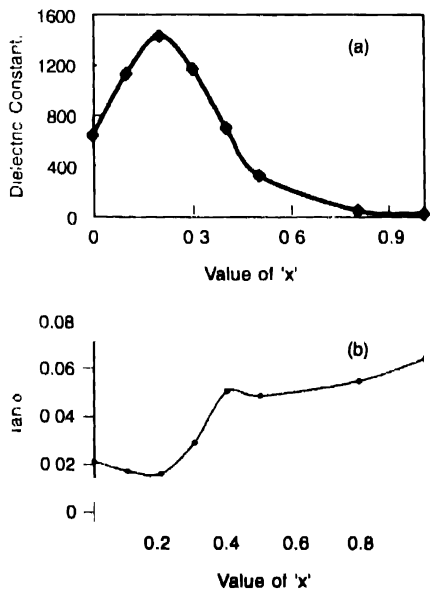

Figure 2. Room temperature variation of dielectric constant and loss tangent with the change of x at 1KHz.

Figure 3 shows a typical variation of ϵ' and $\tan\delta$ with frequency. As evident from the figure, ϵ' shows a slight frequency dispersion at the lower frequency edge. Similar results are expected for displacive type of ferroelectrics as reported by earlier works for $BaTiO_3$ ceramis [7]. The loss tangent shows small frequency dispersion at higher frequencies. However, as we go towards the lower frequency range, $\tan\delta$ shows a monotonous increase. The sharp increase in $\tan\delta$ at lower frequencies may be attributed due to the contribution of d.c. conductivity to the loss tangent.

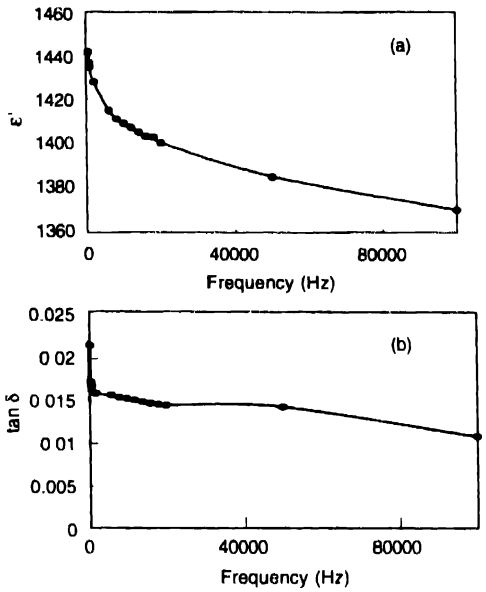

Figure 3. Variation of dielectric constant and loss tangent with frequency of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic

In order to investigate the tetragonal to cubic phase transition, we studied the variation of the dielectric constant and loss tangent with temperature. It was found that there is a systematic shift in the transition temperature with the increase of the value of x. The transition temperatures of different compositions of the ceramics are shown in Table 1. The dielectric constant and loss tangent showed anomaly peaks at the same temperature for a particular composition. The peak values of the dielectric constant for different samples are incorporated in Table 1. All the dielectric anomaly peaks are broad and diffuse, as typically shown in Figure 4. The reason for the broad and diffuse peaks may be attributed to various reasons such as the presence of space charge layers at the electrode-ferroelectric interface and grain boundaries [16], the presence of micrograins with local compositions varying from the average composition [17, 18]. As evident from Figure 4(a), the two anomaly peaks occur at 337k and ≈ -258k. Single crystal barium titanate shows the orthorhombic to tetragonal and tetragonal to cubic phase transitions at 278k and 393k respectively. Sol-gel processed $BaTiO_3$ ceramics also show tetragonal to cubic transition at 398k [7]. The lowering of the transition temperature in our samples may be attributed to the doping of strontium. As evident from Table 1, the samples with $x = 0.3$ shows ferroelectric to

paraelectric phase transition near the room temperature. We expect the sample with ferroelectric to paraelectric phase transition temperature near the room temperature to have the highest value of room temperature dielectric constant. However, samples with $x = 0.2$ which have transition temperature of 337K

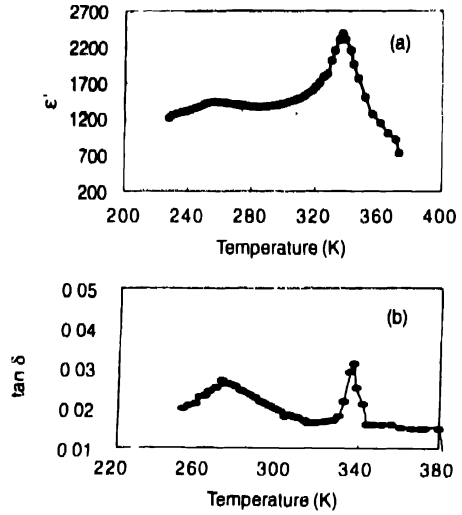

Figure 4. Variation of dielectric constant and loss tangent with temperature of $Ba_{0.8}Sr_{0.2}TiO_3$ ceramic

shows a maximum dielectric constant and minimum loss tangent. The probable reason for this may be that the transition temperature of the sample shifts to higher temperature as some of the tetragonal grains remain locked in the space charge regions at the grain boundaries. As the samples are polycrystalline in nature, the contribution of the grain boundaries on the dielectric properties of the samples may be significant. However, a detailed study on the temperature dependent properties of the samples with different grain boundaries is needed to get a conclusive picture.

4. Conclusion

$Ba_{1-x}Sr_xTiO_3$ ($x = 0.0, 0.1, 0.2, ..., 1.0$) ceramic samples were fabricated by sol-gel processing technique. The samples with $x \leq 0.2$ are tetragonal while those with $x > 0.2$ are cubic in structure. The transition temperature of the compound shifts systematically towards the lower value of temperature with the increase of the value of x. The ceramic with the composition $x = 0.2$ has maximum value of dielectric constant and minimum value of loss tangent at room temperature. All the samples show anomaly peaks which are broader and more diffuse with the increase of the value of x.

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